Carville Barge Monitoring Project

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This report was prepared by the Office of Environmental Assessment, Air Quality Assessment Division in conjunction with the American Waterways Operators.

Contents

Background

The Baton Rouge area is currently classified as being in nonattainment with the 1997 8-hour national ambient air standard for ozone. Ozone is formed in the atmosphere due to a complex interaction between volatile organic compounds and oxides of nitrogen. Petrochemical facilities, automobile emissions, area sources and natural occurring emissions are the most common sources of these ozone causing pollutants. The Louisiana Department of Environmental Quality (LDEQ) has conducted extensive investigations to identify emission sources that may have contributed to some of the ozone exceedances. While the causes for many episodes have been identified, many others still remain a mystery.

Tank barges traveling the nation's river systems transport large amounts of petrochemicals past population centers such as New Orleans & Baton Rouge, Louisiana. Given a hypothesis that fugitive emissions from these vessels may have an impact on local ozone formation, LDEQ has previously undertaken several projects to determine the magnitude of those emission sources through the use of gas imaging cameras and isolated on-barge sampling techniques. Inadvertent emissions have been detected at various areas, such as improperly secured hatches, valve stems and pressure relief valves.

Project Development

In April 2009, LDEQ and the American Waterways Operators (AWO) partnered on this study to determine the impact of barge traffic on air quality in the Baton Rouge area. The study was conducted through the season sensitive to ozone formation (May 1 through September 30). The two parties signed a memorandum of understanding that outlined an in-depth plan to work cooperatively to determine if barges are impacting volatile organic compound readings at the LDEQ's Carville air monitoring site. The Carville site, located at the bend in the Mississippi River south of Baton Rouge near River Mile 190, was selected because its location reports higher annual ozone readings than other monitors in the region. In addition, the Carville site presents a unique geographic and navigational area that would allow the team to pinpoint whether barge or other marine traffic could be directly associated with a monitor trigger.

The plan called for the Carville air monitor to automatically take an emissions sample when volatile organic compounds (VOCs) reached a pre-determined level (400 ppbC VOC). In the event of an emissions trigger above 400 ppbC, LDEQ would alert AWO designated barge industry representatives, who would use Automatic Identification System (AIS)-based software to identify the tank barges operating in the monitored area at the time of the trigger. Then, an AWO-designated industry representative would contact the owner of each barge operating in the area at the time of the trigger and ask: (1) the barge name; (2) whether the barge was loaded or empty; and, (3) the current or (if empty) previous cargo that the barge was or had been carrying. After collecting this information, the AWO-designated representative was tasked with sending it to LDEQ. The AWO and LDEQ could then determine if there was any product moving on the river that may have triggered the VOC sampler.

The primary purpose of this project was to make a scientifically sound determination on whether marine traffic was present in the area when the Carville monitor was triggered, and if emissions from any vessels present could have contributed to the triggering. The methodology DEQ used for this project was the same proven and legally defensible methodology being used nationwide for air pollutants. The resulting monitoring data should have a high standard of quality assurance and validity as set forth in the DEQ Quality Assurance Project Plans for air toxics and ambient air monitoring.

Carville Site Information

EPA AQS Number	220470012					
State	Louisiana					
Parish	Iberville					
City	Carville					
Address	Highway 141					
Site Coordinates UTM	ZONE	15	EAST	681231.077	NORTH	3342862.298
Latitude & Longitude	30° 12' 13.54" N			91° 07' 02.10" W		
Date Sampling Began	July 1976					

Figure 1: Photograph of Carville Air Monitoring Site

Study Focus

The focus of this monitoring project was to:

- Identify the chemical compounds that are most abundantly present in the ambient air in the Carville area.
- Determine from the chemical components present in the samples a set of emission source profiles.
- Determine if any barge or ship traffic was in the area when an air pollution event occurred.
- Determine which if any of the source profiles could be attributed to river sources such as barge or ship traffic.

Sampling & Analytical Methods

Several sampling and analysis strategies were considered in the approach for this project. Ultimately, it was decided to use the triggered auto-gas chromatograph in addition to the 24-hour canister sampler already in place at the site. The composite of the 24-hour samples could be used to determine the "normal" air quality at the site, while the triggered samples were used to demonstrate high VOC pollution events or "worst case" air quality.

All of the canister sampling and analysis was conducted using Method TO-15 of the U.S. Environmental Protection Agency's "Compendium to the Determination of Toxic Organic Compounds in Ambient Air." This method involves the collection of air samples in specially prepared stainless steel canisters with subsequent analysis using gas chromatography techniques with Flame Ionization Detectors (FID) and Mass Spectrometry Detectors (MSD). The samples were analyzed in the LDEQ laboratory for nearly 100 VOCs.

In order to determine compliance with Louisiana's ambient air standards, the site uses a statistical canister sampler operating on a 24-hour/once every 6^{th} day schedule. The sampler runs from midnight on the scheduled sampling day until midnight on the following day. Sampling was conducted with a Model 911A Portable Summa Canister manufactured by RM Environmental Systems Incorporated. The sampler was configured to collect the samples following the statewide air toxics sampling schedule.

The site was equipped with a continuous methane/non-methane hydrocarbon analyzer consisting of a TECO model 55C. When a 10 minute average concentration exceeded the set trigger level (usually 400 ppbC), the data logger activated the gas chromatograph which collected a 25 minute duration sample which was analyzed for 55 ozone producing chemical compounds. The 400 ppbC trigger level was chosen based upon historical data that would trigger the instrument an estimated 12 times per month. The Gas Chromatograph system used was a Perkin-Elmer Ozone Precursor system, which consists of a concentrator/thermal desorption unit coupled to a dual column gas chromatograph. The methodology used for this analysis followed the U.S. Environmental Protection Agency's reference method for ozone precursor monitoring in ambient air.

All continuous monitoring data collected was stored on a data logger which recorded the hourly and 5-minute average concentration of each pollutant. Hourly wind speed and direction data was also collected and recorded on the data logger.

Whenever the monitor was triggered by a high hydrocarbon reading, barge industry representatives would reference ShipTracks, an AIS-based commercial vessel tracking system to reveal the river traffic in the vicinity of the monitor (River Mile 188 to River Mile 200). The companies that own the barges in the area were contacted and asked what product was being shipped in their respective barges.

All of the analytical data was compiled and processed using the Positive Matrix Factorization receptor model. Positive Matrix Factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices—factor contributions and factor profiles—which then need to be interpreted by an analyst as to what source types are represented using measured source profile information, wind direction analysis, and emission inventories.

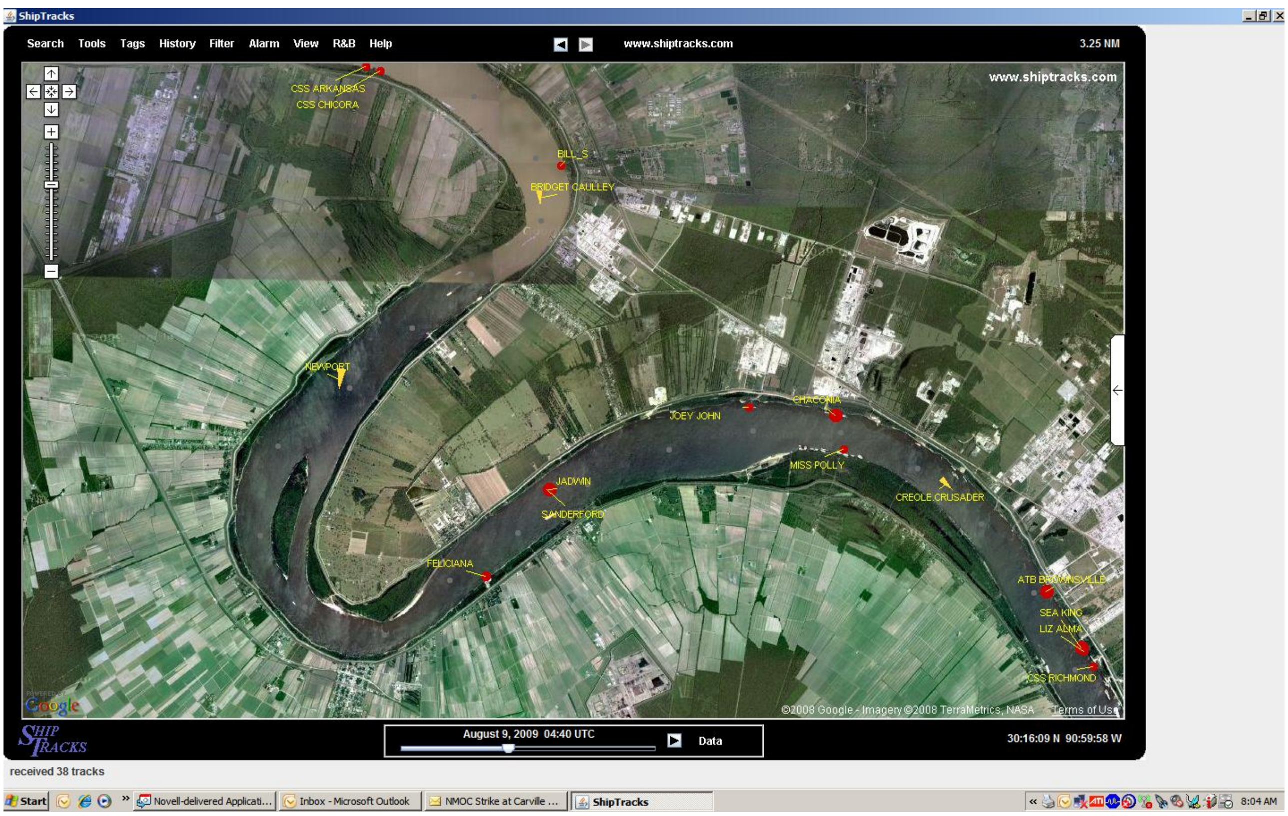

Figure 2: A Map of the Carville Air Monitoring Corridor showing river traffic

Analytical Results - Twenty-four Hour Samples

For the purposes of the study, 24-hour canister samples collected between January 1, 2008, and September 30, 2009, were examined for comparative purposes. Most of the targeted compounds were detected within the typical concentration range of 0.1 to 25.0 ppb, and were generally at or below the statewide averages. All of the average concentrations for the toxic compounds are in compliance with the Louisiana Ambient Air Standards, and 95 percent confidence intervals were calculated for each of the targeted compounds. The upper limits of the confidence intervals were also well below the Ambient Air Standards.

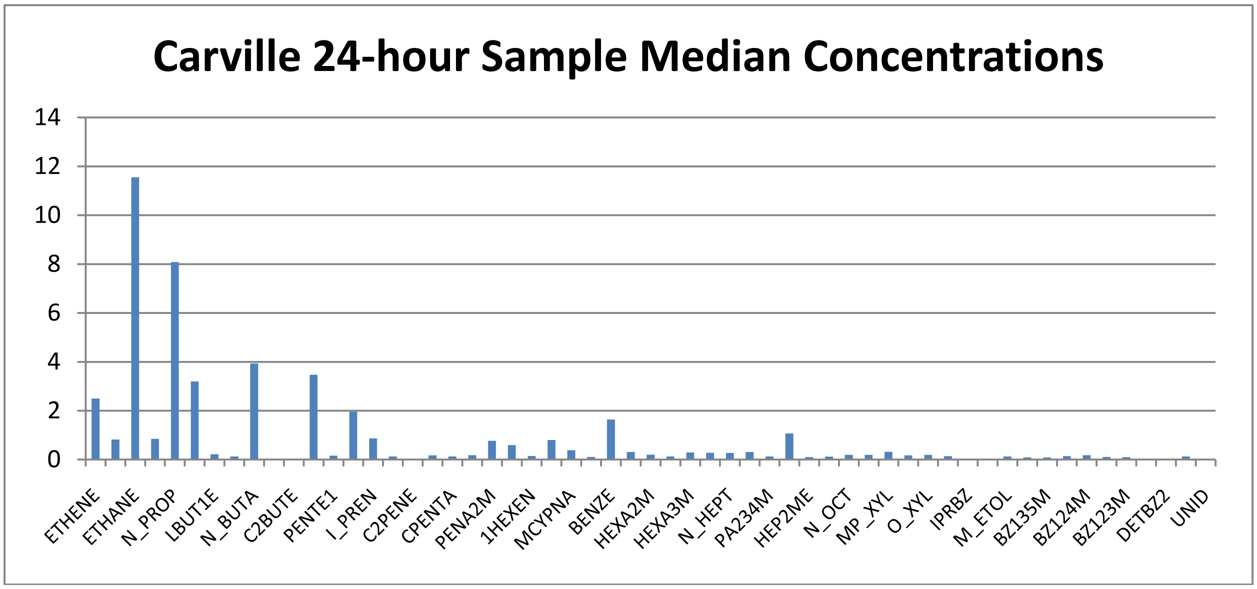

Figure 3: Carville Monitoring Site 24-hour Sample Median Concentrations (in ppbC)

All of the canister data was also compared to the Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs). An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure. These substance specific estimates, which are intended to serve as screening levels, are used by ATSDR health assessors and other responders to identify contaminants and potential health effects that may be of concern at hazardous waste sites. **It is important to note that MRLs are not intended to define clean up or action levels for ATSDR or other Agencies.** None of the readings observed at the site exceeded any of the ATSDR Minimal Risk levels for a short-term (acute) exposure.

Triggered Auto Gas Chromatograph Samples

A total of 76 triggered samples were collected in the study. The results for these samples were highly variable depending mostly on the wind direction at the time of collection and the source of the emissions which triggered the sampler. The concentrations in these samples represent the likely maximum "worst case" concentrations of the various toxic air pollutants.

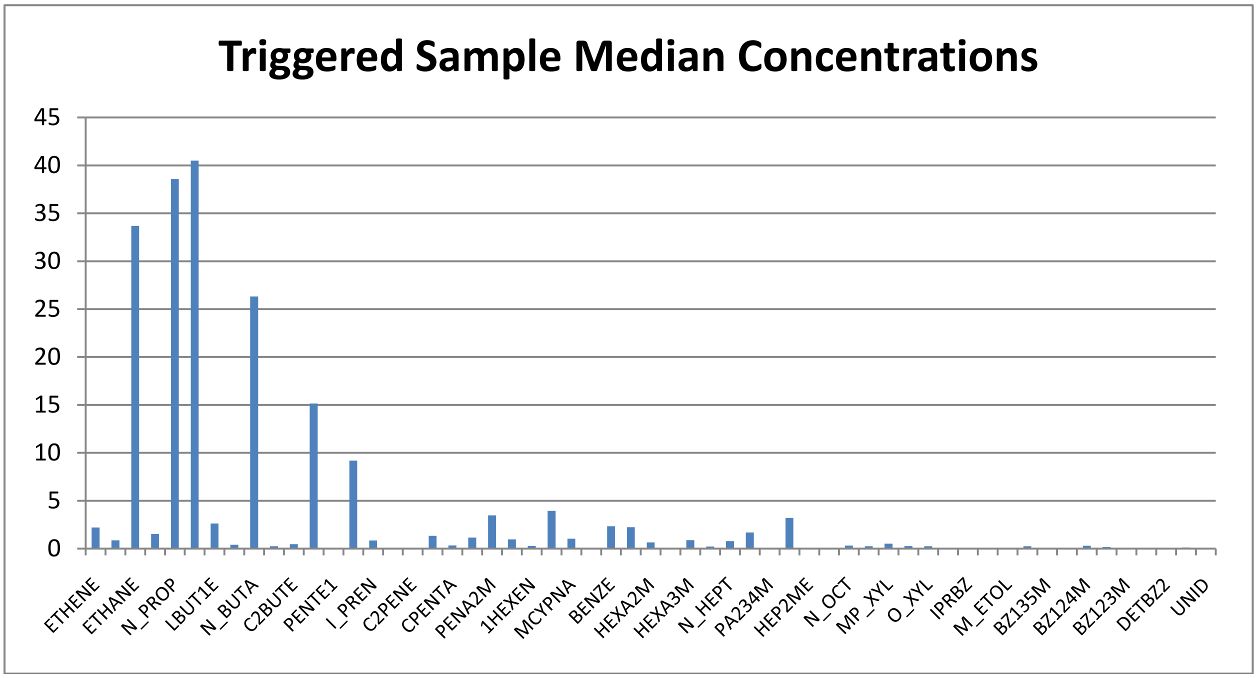

Figure 4: Carville Monitoring Site Triggered Sample Median Concentrations (in ppbC)

PMF Modeling Results

Receptor modeling is a mathematical procedure for identifying and quantifying the sources of ambient air contaminants at a receptor, primarily on the basis of ambient concentration measurements. Multivariate receptor models require the input of data from multiple samples and extract the source information from all of the sample data. The models estimate not only the source contributions but also the source compositions (profiles).

Exploratory source apportionment of the Carville 24-hour and auto-GC data was performed to explore possible emission source types of VOCs along the Mississippi river. Positive Matrix Factorization (PMF) receptor modeling was used to identify likely sources. The model provides emission profiles which can be related to emission source types and which estimate the quantitative contribution of each factor in every sample. Thus, the variation of source strength by time of day, day of week, and wind direction can be explored

The 24-hour data and the triggered data were modeled separately to determine which emission factors were the most influential in each data set. PMF analysis of the 24-hour data identified eight factors over the entire data set. PMF analysis of the triggered auto-GC data set also identified eight factors but several of factors were quite different suggesting new source types causing some of the triggered samples.

PMF Analysis of 24-hour samples

Profile	Contribution	Key Species	Likely Source
1	29%	Ethane & Propane	Background Accumulation
2	8%	Isopentane, Pentane & Toluene	Mobile sources
3	6.7%	Isoprene	Biogenic
4	8.8%	Ethylene, Propylene & Toluene	Heavy duty mobile (diesel)
5	9.8%	Benzene, Ethane, Propane & Butane	Industrial
6	14%	n-butane & n-propane	Evaporative fuel (gasoline)
7	14.3%	Isobutane & n-propane	Industrial
8	8.7%	Ethane & Propylene	Industrial

PMF Analysis of the Triggered Auto GC Samples

Profile	Contribution	Key Species	Likely Source
1	5.3%	n-hexane & methylcyclopentane	not determined
2	8.0%	Isobutane & n-propane	Industrial
3	14.4%	Isopentane & n-pentane	Evaporative fuel
4	3.6%	1-butene,Isopentane, Pentane & Toluene	Mobile sources
5	9.3%	Cyclohexane	not determined
6	35.4%	Isobutane & n-propane	Industrial
7	12.0%	Ethane & Propane	Background Accumulation
8	5.7%	Totuene, Isopentane & n-pentane	Mobile sources & Evaporative fuel

The industrial sources identified in the 24-hour samples and background accumulation accounted for the vast majority of the triggered samples and nearly half of the total mass contributions. When these triggers occurred there often were no river sources or barge traffic in the area.

A small number of the triggered samples appeared to be unique and could possibly be attributed to river sources. The evaporative fuel profile appeared in several samples and did occur when the wind direction was from the river. This profile was very similar to some samples collected in the Baton Rouge barge study conducted in September 2008.

One triggered sample consisting of this profile occurred on 7/20/2009 at 1:40 p.m. The winds at the time were out of the south at 5 mph. When the river traffic information provided by the American Waterway Operators was examined, a barge carrying natural gasoline was in a position directly upwind of the monitoring station.

Another trigger consisting of this profile occurred on 5/31/2009 at 9:30 a.m. The wind direction was from the south-southeast at 3 mph. When the river traffic information provided by the American Waterway Operators was examined, a barge carrying what was labeled as benzene and toluene was in the area. However, based on the wind direction, the barge would not have impacted the monitor. A chemical cargo ship was anchored south of the monitor, but its specific cargo was unknown.

A few triggers of the profiles containing either cyclohexane or hexane were also noted. One such triggered sample occurred on 7/26/2009 at 5:50 a.m. The wind was out of the south-southeast at 2 mph. When the river traffic information was examined, it noted a set of barges carrying what was described as “styrene and used oil” was located west of the site. Movement from those barges indicated that they had passed by the site earlier. Several other triggers containing cyclohexane or hexane were observed, but no barges containing cyclohexane or hexane were observed in the monitoring corridor during the time of the triggers. These events underscore some of the difficulty in matching observed chemical profiles with the described cargo. When examining some of the emission profiles provided by the EPA Speciate database, it was observed the evaporative emission profiles for many cargos (such as crude oil or diesel) looked very different than the bulk contents chemical profile.

Conclusions

The conclusion of this initial study is that approximately five percent of triggered samples could be attributed to barge, ship or other river sources. This seems to be consistent with past observation at the Carville site when a small number of triggered samples occurred each year. The samples had chemical profiles not matching industrial profiles or normal background composition. While the contribution from barges or other river traffic appears to be very small in the overall amount of VOCs present, the periodic elevated VOC levels could contribute to some localized elevated ozone levels. The average levels of VOC are consistent with the levels observed in most other rural areas of the state where the VOC profiles are dominated by background, biogenics and mobile source emissions. Most of the triggered samples could be attributed to background accumulation or influence from local industrial sources. While this study does not directly correlate tank barge emissions to ozone exceedance days, it would be prudent to continue studying potential sources of ozone precursors to better understand the true cause of the ozone levels at the Carville monitor and Baton Rouge areas.

Next Steps

Several options are under consideration by DEQ & the AWO for the pathway of future study. The options being considered are:

- Continue monitoring barge and river traffic at the Carville Station.
- Move the equipment and monitor barge and river traffic at other locations such as those discussed near L.S.U. in Baton Rouge or in the Lake Charles area..
- Design a new monitoring effort and deploy the equipment at a location to be designated later.

After further evaluation, LDEQ staff and AWO members will determine the optimal next step for future study.

Appendix

24 Hour Canister Sample Statistics (all values in ppbC)

Species	Min	25th	Median	75th	Max
ETHENE	0.31	1.51	2.50	4.82	16.11
ACETYL	0.00	0.57	0.82	1.28	3.51
ETHANE	0.27	8.76	11.55	17.72	53.29
PROPE	0.00	0.40	0.85	1.66	10.99
N_PROP	0.00	6.34	8.08	12.23	24.78
I_BUTA	0.65	2.04	3.20	5.40	35.75
LBUT1E	0.00	0.16	0.22	0.42	14.66
13BUTD	0.00	0.08	0.13	0.24	1.53
N_BUTA	0.62	2.67	3.93	6.80	21.41
T2BUTE	0.00	0.00	0.00	0.00	41.26
C2BUTE	0.00	0.00	0.00	0.00	0.55
IPENTA	0.71	2.15	3.47	4.52	33.05
PENTE1	0.00	0.11	0.16	0.22	2.76
N_PENT	0.61	1.34	1.96	3.00	12.93
I_PREN	0.00	0.37	0.87	1.91	6.30
T2PENE	0.00	0.00	0.13	0.20	1.34
C2PENE	0.00	0.00	0.00	0.10	0.55
BU22DM	0.00	0.11	0.17	0.22	0.77
CPENTA	0.00	0.09	0.13	0.18	1.49
BU23DM	0.00	0.13	0.18	0.27	2.16
PENA2M	0.17	0.54	0.77	1.20	6.29
PENA3M	0.00	0.37	0.59	0.85	8.28
1HEXEN	0.00	0.00	0.15	0.30	1.15
N_HEX	0.00	0.65	0.80	1.47	5.20
MCYPNA	0.00	0.25	0.38	0.61	2.81
PEN24M	0.00	0.08	0.11	0.15	0.64
BENZE	0.26	1.06	1.64	2.62	19.05
CYHEXA	0.00	0.21	0.31	0.51	2.16
HEXA2M	0.00	0.15	0.20	0.30	1.12
PEN23M	0.00	0.10	0.13	0.17	0.86
HEXA3M	0.00	0.20	0.29	0.40	1.28
PA224M	0.00	0.19	0.28	0.46	2.20
N_HEPT	0.00	0.21	0.27	0.39	1.09
MECYHX	0.00	0.22	0.31	0.40	1.12
PA234M	0.00	0.08	0.13	0.18	0.72
TOLUE	0.25	0.72	1.07	1.77	7.33
HEP2ME	0.00	0.00	0.10	0.13	0.74
HEP3ME	0.00	0.00	0.12	0.18	0.47
N_OCT	0.00	0.13	0.19	0.25	0.77
ETBZ	0.00	0.12	0.19	0.41	1.82
MP_XYL	0.00	0.22	0.32	0.53	2.01
STYR	0.00	0.09	0.17	0.39	3.74
O_XYL	0.00	0.11	0.19	0.24	1.02
N_NON	0.00	0.09	0.14	0.17	0.56
IPRBZ	0.00	0.00	0.00	0.13	0.98
N_PRBZ	0.00	0.00	0.00	0.09	0.60
M_ETOL	0.00	0.00	0.13	0.17	0.82
P_ETOL	0.00	0.00	0.09	0.12	0.70

Species	Min	25th	Median	75th	Max
BZ135M	0.00	0.00	0.09	0.14	0.62
O_ETOL	0.00	0.00	0.14	0.19	0.66
BZ124M	0.00	0.12	0.18	0.31	14.86
N_DEC	0.00	0.07	0.11	0.15	1.06
BZ123M	0.00	0.00	0.10	0.26	4.25
DETBZ1	0.00	0.00	0.00	0.08	0.69
DETBZ2	0.00	0.00	0.00	0.09	0.57
N_UNDE	0.00	0.09	0.13	0.16	0.96
UNID	5.23	32.80	45.92	66.54	187.29
TNMOC	38.00	78.00	110.00	147.00	249.00

Triggered Sample Statistics (all values in ppbC)

Species	Min	25th	Median	75th	Max
ETHENE	0.00	0.34	2.21	9.37	43.86
ACETYL	0.00	0.37	0.88	1.67	7.44
ETHANE	3.73	20.89	33.69	59.66	202.89
PROPE	0.00	0.74	1.54	5.81	93.60
N_PROP	3.27	24.98	38.58	56.77	165.17
I_BUTA	0.00	12.60	40.49	75.51	289.88
LBUT1E	0.00	0.99	2.63	6.33	31.67
13BUTD	0.00	0.04	0.40	0.55	11.58
N_BUTA	1.54	11.16	26.32	44.02	138.33
T2BUTE	0.00	0.00	0.25	0.51	16.02
C2BUTE	0.00	0.15	0.47	1.20	17.55
IPENTA	0.00	5.02	15.16	34.24	389.68
PENTE1	0.00	0.00	0.00	0.00	14.23
N_PENT	0.00	3.16	9.18	18.74	254.17
I_PREN	0.00	0.00	0.86	2.35	5.10
T2PENE	0.00	0.00	0.00	0.00	22.35
C2PENE	0.00	0.00	0.00	0.00	12.85
BU22DM	0.00	0.52	1.35	2.48	11.32
CPENTA	0.00	0.00	0.34	0.67	34.26
BU23DM	0.00	0.38	1.16	2.70	51.56
PENA2M	0.00	1.51	3.48	7.01	98.85
PENA3M	0.00	0.00	0.98	4.84	18.24
1HEXEN	0.00	0.00	0.29	0.73	3.19
N_HEX	0.38	2.45	3.95	9.58	48.70
MCYPNA	0.00	0.28	1.05	4.15	35.26
PEN24M	0.00	0.00	0.00	0.00	7.90
BENZE	0.30	1.46	2.35	3.68	44.15
CYHEXA	0.00	0.61	2.25	8.40	441.40
HEXA2M	0.00	0.00	0.66	1.26	19.19
PEN23M	0.00	0.00	0.00	0.48	8.95
HEXA3M	0.00	0.60	0.89	1.48	21.84
PA224M	0.00	0.00	0.22	0.92	13.86
N_HEPT	0.00	0.50	0.79	1.55	16.09
MECYHX	0.00	0.79	1.70	3.21	8.99
PA234M	0.00	0.00	0.00	0.00	3.20
TOLUE	0.93	2.41	3.20	4.05	62.98
HEP2ME	0.00	0.00	0.00	0.26	4.24
HEP3ME	0.00	0.00	0.00	0.25	4.49
N_OCT	0.00	0.00	0.32	0.55	3.88
ETBZ	0.00	0.00	0.25	0.56	6.51
MP_XYL	0.00	0.20	0.52	0.69	14.69
STYR	0.00	0.00	0.28	0.71	14.28
O_XYL	0.00	0.00	0.25	0.36	5.05
N_NON	0.00	0.00	0.05	0.27	0.80
IPRBZ	0.00	0.00	0.00	0.00	1.88
N_PRBZ	0.00	0.00	0.00	0.00	1.00

Species	Min	25th	Median	75th	Max
M_ETOL	0.00	0.00	0.00	0.00	2.90
P_ETOL	0.00	0.00	0.26	0.43	1.37
BZ135M	0.00	0.00	0.00	0.00	1.15
O_ETOL	0.00	0.00	0.00	0.00	1.30
BZ124M	0.00	0.14	0.31	0.51	5.76
N_DEC	0.00	0.00	0.17	0.25	0.56
BZ123M	0.00	0.00	0.00	0.20	1.82
DETBZ1	0.00	0.00	0.00	0.00	0.38
DETBZ2	0.00	0.00	0.00	0.00	0.80
N_UNDE	0.00	0.00	0.13	0.25	1.42
UNID	6.73	15.15	22.14	43.32	282.67
TNMOC	106.00	204.00	302.50	415.00	1631.00